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(54) Fluorination of organic compounds with fluorine in porous metal tube reactor with perfluorinated diluent.

(57) An acyclic organic compound such as acetone, ethane or propane having at least one fluorinatable is introduced outside a porous metal member, while gaseous fluorine is introduced with the porous metal member. At least one of the reactants is diluted with a perfluorinated gaseous diluent such as sulfur hexafluoride. The process is applicable to the production of octafluoropropane.

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DESCRIPTION

FLUORINATION OF ORGANIC COMPOUNDS WITH FLUORINE IN POROUS METAL TUBE REACTOR WITH PERFLUORINATED DILUENT

BACKGROUND OF THE INVENTION

This invention relates to the fluorination of organic compounds with elemental fluorine and particularly to the fluorination of organic compounds in a porous tube reactor wherein fluorine is fed onto one side of a porous member and the organic compound is fed onto the other side of the porous member, fluorine migrates through the porous member and fluorinated products are recovered from the other side of the porous member.

The direct fluorination of organic compounds using elemental fluorine as a reactant, especially where the organic compound contains a carbon backbone of two or more atoms, has been considered impractical. Thus standard texts indicate the reaction $R-H+X_2 \rightarrow R-X+HX$ to be satisfactory only when X is Cl or Br and not when X is F. Especially where R has more than one carbon, a substantial proportion of products having a different number of carbons than the reactants has been produced. Thus, for example, in the literature reports in volumes 61, 62 and 63 of the Journal of the American Chemical Society by L. A. Bigelow, yields with methane, ethane and acetone of CF_4 , C_2F_2 and CF_3COCF_3 were, respectively, 30-50%, 30-40% and 10%. Intermediates and by-products for methane included $CH_{1-3}F_{3-1}$, C_2F_6 and C_3F_8 . Intermediates and byproducts for ethane included $C_2H_{1-5}F_{5-1}$, $CH_{1-3}F_{3-1}$, C_2F_6 and CF_4 (the latter resulting from

cleavage of a carbon carbon bond). Intermediate and byproducts for acetone included CF_4 , COF_2 , CF_3COF , $(\text{COF})_2$ and $\text{CH}_3\text{COCH}_2\text{F}$.

An invention of Bruce E. Kurtz, described in Canadian Patent 990,738 issued June 6, 1976 and also described in a somewhat different form in copending, commonly-assigned U.S. Patent Application 644,788 filed December 29, 1975 (now U.S. Patent 4,187,253, issued February 5, 1980), includes the chlorination of one and two carbon hydrocarbons and their partially chlorinated derivatives in a porous tube reactor. In these references the porous tube is an elongated member, preferably of fritted Pyrex glass (Pyrex being a registered trademark), but also permissibly of Alundum (a registered trademark for a fixed alumina refractory material), a ceramic or a sintered metal, being in each case resistant to chlorine, anhydrous HCl , and the feed and product organic and chlorinated organic compounds.

Two Japanese patents disclose the fluorination of organic compounds in a solvent with fluorine, using sulfur hexafluoride as a diluent for the fluorine. In Kokai 49000,201 (January 5, 1974) (Chemical Abstracts 80:95458n) non-polymeric organic compounds such as C_6H_6 , toluene and uracil were used as reactants with the corresponding monofluorocompounds produced. In 49046281 (December 9, 1974) (Chemical Abstracts 82:1731689) carbon and fluorine in the presence of SF_6 produced " $(\text{CF})_m$ " polymer and CF_4 as a minor by-product.

Various processes have been proposed for electrochemical chlorination and fluorination of organic compounds. Organic compounds dissolved in or bubbled into anhydrous HF or molten fluoride salt- HF combinations (e.g. KF-2HF) are subjected to an electrolytic voltage, forming elemental fluorine at the anode which fluorinates the product. U.S. Patents 2,841,544 and 3,298,940 describe such a process with a porous or foraminiferous anode, preferably made of carbon. In various Phillips Petroleum Company patents, the

organic material is fed into the porous carbon anode and elemental fluorine passed from the electrolyte at the anode surface (where it is formed) into the porous carbon anode. Helium is sometimes used as a diluent.

5 The present invention relates to the production of perfluoropropane or octafluoropropane which is known to be useful in plasma etching of electronic components and is a dielectric gas.

10 The production of perfluoropropane has been attempted from a variety of starting materials, but no process has been developed which produces the material in high yields without a multitude of steps. Exemplary starting materials are propane, propene, hexafluoropropene and partially halogenated propanes and propenes.

15 U.S. Patent 4,158,023 to von Halasz describes the production of perfluoropropane from hexafluoropropene in two steps. This reference indicates that the direct conversion with elemental fluorine results in poor yields. Since hexafluoropropene is itself fairly
20 hard to produce in good yields, the overall process becomes involved with a multitude of steps and expense.

 U.S. Patent 3,840,445 to Paul et al. describes electrochemical fluorination of propane to perfluoropropane. The reference indicates the difficulty in separating propane from the product by distillation, and,
25 accordingly, employs a two-step process of electrochemical fluorination. Although the product need be separated only from partially fluorinated propane when the two steps are used, the process thereby becomes more
30 involved, and the potential for overall yield losses increases.

 The production of perfluoropropane from propane by elemental fluorination in a jet reactor has been described in an article by A. F. Maxwell et al. in
35 Journal of the American Chemical Society, Vol. 52, pp. 5827-30 (November 20, 1960). The tables in this article report production of perfluoropropane which suggests a yield, in the best case, of about 50 percent

based on propane fed.

BRIEF DESCRIPTION OF THE INVENTION

The present invention includes a process of fluorinating acyclic organic compounds which comprises:

5 a) passing fluorine as a first gaseous reactant into an elongated inner zone surrounded by a porous metal member which is substantially resistant to fluorine corrosion, and

10 b) introducing as a second gaseous reactant outside the porous metal member an organic compound having 2-4 carbons with at least one fluorinatable carbon selected from the group consisting of carbons covalently
15 bonded to H, Cl or Br and carbons olefinically or acetylenically bonded to other carbons;

 the pressure in said elongated inner zone being greater than the pressure outside the porous metal member;

20 at least one of said first and second gaseous reactants being admixed with a perfluorinated gaseous diluent selected from the group consisting of sulfur hexafluoride, tetrafluoromethane, hexafluoroethane and
25 octafluoropropane.

 It has been discovered that the combination of a porous metal tube and the use of a perfluorinated diluent such as sulfur hexafluoride enables such fluorinations to occur with a maximum yield of perfluorinated
30 products of like carbon number and a minimum degree of cleavage products with lesser carbon numbers.

 A preferred class of organic compounds are those with three carbons, such as propane, propene or hexafluoropropene, with the product octafluoropropane
35 being recovered from the effluent outside the porous member.

DETAILED DESCRIPTION OF THE INVENTION

The present invention employs a porous metal

tube for the elemental fluorination of organic compounds. When using such a tube for fluorination, unlike the fluorinations described in Canadian Patent 990,738 and U.S. Patent 4,187,253, it is not sufficient to employ
5 common inert diluents such as nitrogen and achieve good yields with low losses to cleavage reactions or carbon formation. Instead it has been found that a perfluorinated diluent such as sulfur hexafluoride is required. Other perfluorinated diluents such as CF_4 , C_2F_2 or C_3F_8 ,
10 which may also be the reaction product, may be employed in place of sulfur hexafluoride. Alternatively, HF, the reaction byproduct, may be used as a diluent. SF_6 is preferred.

The organic compound used as a second gaseous
15 reactant shall have at least two carbons, at least one of which is "fluorinatably," by which is meant having an H, Cl or Br attached that can be replaced by F or an olefinic or acetylenic bond to another carbon that can be added across by fluorine. Acyclic and cycloaliphatic
20 compounds are preferred over aromatic compounds. Compounds having at least one C-H bond are preferred over compounds having only fluorinatable carbons other than carbons bonded to hydrogen. While carbons bonded to "hetero" atoms such as Br, Cl or O are eventually
25 fluorinated, the present process can also be made selective by using limited amounts of fluorine and/or mild conditions so as to preserve hetero atoms and replace only hydrogens and unsaturations by fluorine.

One preferred group of second reactants are
30 the aliphatic hydrocarbons of at least two carbons, including aliphatic hydrocarbons such as ethane, propane, butane and higher members of the series and olefinic hydrocarbons such as ethene, propene, butene and higher members of the series. Eight carbons is the highest
35 preferred size of the hydrocarbons. These materials can be converted to the corresponding perfluoroalkanes of the formula C_nF_{2n+2} , or less fluorinated members having unsaturations or hydrogens, and less than $2n+2$ F's.

Propane and propene are two preferred reactants in this group.

Another preferred group of second reactants are partially halogenated compounds of the above group having some or all of the hydrogens or unsaturations replaced by Cl, Br or F, but not all by F. Only hydrogens and unsaturations of such reactants are replaced by fluorine under mild conditions, especially temperature, and when the amount of fluorine is limited to that required for the desired fluorination. Thus C_2H_5Cl can be converted to C_2ClF_5 with low temperatures and only five moles of fluorine per C_2H_5Cl ; or it can be converted to C_2F_6 with six or more moles of fluorine per C_2H_5Cl . Hexafluoropropene is a preferred reactant in this group.

Another preferred group of reactants are the ketones of 3-8 carbons such as acetone, methyl ethyl ketone and higher members of the series, together with partially halogenated ketones, as described above. In general hydrogens will first be replaced by fluorine, then Br, then Cl and only then the carbonyl oxygen. Preferred is acetone and partially halogenated acetone.

Another preferred group of second gaseous reactants are the cyclized form of any of the above such as cyclopentane, cyclohexane, and cyclohexene. In general, aromatics are not preferred since they are more likely to result in byproducts which can clog the pores of the porous tube.

Either the first or second gaseous reactant can be mixed with the perfluorinated diluent, such as sulfur hexafluoride. Preferably, both reactants are mixed with sulfur hexafluoride. The mole ratio of fluorine to sulfur hexafluoride admixed therewith is preferably between about 2:1 and about 1:12, more preferably between 1:5 and about 1:10. The mole ratio of second gaseous reactant to sulfur hexafluoride admixed therewith is preferably between about 4:1 and about 1:5, more preferably between about 1:1.5 and about 1:3.

The ratio of fluorine to three carbon compound

depends, in part, upon the particular three carbon compound employed. Thus, in general, one can compute the stoichiometric amount of fluorine required to convert the entire second reactant to a perfluoropropane as a first estimate of the desired amount of fluorine to be introduced.

For three carbon compounds having a hydrogen, one mole of fluorine is required for each mole of hydrogen bonded to carbon such that half of the fluorine molecule can replace the hydrogen to form a C-F bond and the other half of the fluorine molecule can form HF by-product. For each unsaturation, one mole of fluorine is required to add across a double bond and to form two C-F bonds. For each other halogen present such as Cl or Br, or any other hetero atom present, one molecule of fluorine is generally required to both replace the hetero atom and form a by-product between fluorine and the hetero atom. In general, however, hetero atoms are preferably not present such that the three carbon compound has no elements other than carbon, hydrogen and fluorine.

While any amount of fluorine may be used, it is preferred to use between 50 and 150 percent of the stoichiometric amount. Thus, in the case of propane, 8 moles of fluorine per propane constitutes the stoichiometric amount, and a generally suitable range of fluorine is between about 4 and about 12 moles of fluorine per propane. Preferably, between about 5 and about 10 moles of fluorine are introduced into the inner zone per mole of propane introduced outside the elongated porous member. More preferably between about 8 and about 9.5 moles of fluorine are introduced per mole of fluorine.

In the case of propene, the stoichiometric amount is 7 moles of fluorine per propene. A generally suitable overall range is between about 3.5 and about 10.5 moles of fluorine per mole of propene. A preferred range of fluorine to propene ratios is between about 4:1 and about 8:1, more preferably between about

7:1 and about 8:1.

In the case of hexafluoropropene, the stoichiometric mole ratio is 1:1 while a range of about 0.5:1 to about 1.5:1 is suitable, as well as amounts higher, and especially lower in fluorine than that range, the preferred ratios are between about 0.7:1 and about 1.1:1, especially about 1:1.

The porous tube used in the present invention can be any metal inert to corrosion by fluorine under the relatively mild reaction conditions employed. Preferably the pore size is between about 0.5 and about 50 micrometers, taken as an average of all pores or as a limitation on substantially each and every pore.

Where propane is the reactant, octafluoropropane can be recovered from the effluent by condensing the effluent under sufficiently high pressure and low temperature to condense octafluoropropane, separating the condensate from the uncondensed portion of the effluent, separating an organic phase of the condensate from a hydrogen fluoride phase of the condensate and recovering octafluoropropane from the organic phase of the condensate. The preferred method of recovering octafluoropropane from the organic phase of the condensate is by fractional distillation since, once phase separation has occurred, no compounds boiling close to octafluoropropane will remain in the condensate. It should be appreciated that, if propane itself were present in the effluent, it would also be found in the organic phase of the condensate and would, according to U.S. Patent 3,840,445 complicate purification. In the examples described below having a stoichiometric excess of fluorine, no propane was detected in the effluent and no difficulty should be encountered in separating perfluoropropane from other materials by fractional distillation.

Example 1 - Fluorination of Ethane

Fluorine gas (0.1 mol/h) admixed with sulfur hexafluoride (0.50 mol/h) was introduced at 101.4 kPa

pressure into the bottom of a 6 inch (15.2 cm) long, 1.5 inch diameter Inconel porous tube of wall thickness 0.065 inch (.165 cm) thickness and 10 micrometer pore size (Inconel being a registered trademark for a nickel-ironchromium alloy). The tube was sealed at the top. Ethane (0.40 mol/h) was introduced at a pressure of 101.4 kPa into a 1/2 inch (1.27 cm) by six inch (15.3 cm) annular zone outside the porous tube and inside a concentric impervious stainless steel tube 2 inches (5.08 cm) in diameter. Gaseous effluent was removed from the top of the annular zone. Thus total feeds were 0.10 mol/h F_2 , 0.40 mol/h of C_2H_6 and 0.50 mol/h of SF_6 . The temperature was monitored by a thermowell along the outside of the porous tube and showed a maximum of 76°C at a calculated contact time of 20 seconds. On-line gas chromatographic analysis of the effluent, after passing through a sodium fluoride bed to absorb the HF, showed about .013 mol/h C_2F_6 (80% yield based on F_2 feed), about .005 mol/h CF_4 (20% yield based on F_2 feed) and no partially fluorinated ethanes such as C_2HF_5 or C_2H_5F .

A similar experiment using nitrogen as the diluent produced only CF_4 , the cleavage product, and no measurable C_2F_6 . In this experiment the maximum temperature sensed by the thermowell was 75°C. Even when the reaction temperature was lowered to -50°C by a cooling bath only CF_4 was observed in the effluent. Those two runs are described in more detail as Comparative Examples 15 and 16, below.

Examples 2-4 - Fluorination of Propane and Propene

Example 1 was repeated using the same tube, but now feeding 0.25 or 0.50 mol/h of F_2 admixed with 2.0 mol/h of SF_6 into the bottom of the porous tube and 0.25 mol/h of propane or propene admixed with 0.50 mol/h of SF_6 into the annular zone, all as shown in Table 1. On-line gas chromatographic analysis of the vaporized effluent gave the area percentages shown in Table 1.

Table 1

Example Feeds		Fluorination of C ₂ -3 Hydrocarbons			4
	C-3 Organic (0.25 mol/h)	propene	propane	propane	
5	SF ₆ (mol/h) annular zone	2.0	2.0	2.0	
	F ₂ (mol/h)	0.25	0.25	0.50	
	SF ₆ (mol/h) inside tube	0.50	0.50	0.50	
	CF ₄ (area %)	3	0	3	
	C ₃ F ₈ (area %)	18	18	58	
10	C ₃ H ₁₋₇ F ₇₋₁ * (area %)	79	82	39	
	C ₃ F ₈ yield (based on F ₂)	18	17	54	

*together with similar partially fluorinated hexanes

Example 5 - Fluorination of Acetone

Using the apparatus of Example 1, 0.25 mol/h

- 15 of fluorine admixed with 2.0 mol/h of sulfur hexafluoride was admitted into the porous tube and 0.30 mol/h of acetone and 0.60 mol/h of sulfur hexafluoride was admitted to the annular zone. This reaction was continued for ten hours with the effluent passing
- 20 through an NaF scrubber to remove HF by absorption and then trapped in condenser traps at -80°C and -196°C. The temperature profile measured by the thermowell along the surface of the porous tube under steady state conditions was 117°C at the base, 139°C two inches (5
- 25 cm) from the base, 141°C four inches (10 cm) above the base and 125°C at the top of the tube six inches (15 cm) above the base. The thermowell measured 73°C two inches (5 cm) above the upper end of the porous tube.

- The trapped materials were combined into one
- 30 cylinder which contained 100 g of water. The purpose of the water was to complex the fluoroacetones as their hydrates which could then be isolated by distillation. After venting off the more volatile SF₆, the recovered aqueous organic mixture which was composed of unreacted
- 35 acetone, H₂O and fluoroacetone hydrates was distilled. The comparative results of distillation and gas chromatographic analysis of the aqueous organic mixture (expressed as the anhydrous products) are shown in

Table 2.

Table 2
Fluorination of Acetone

	<u>Distillation</u>	<u>Gas Chroma- tography</u>
5		
Hexafluoroacetone Yield %	36.8	50.2
Pentafluoroacetone	3.6	2.1
Tetrafluoroacetone (sym)	0.4	7.4
Difluoroacetone (sym)	0.1	-
10		
Monofluoroacetone	4.6	6.7
Total Yield (F ₂ Basis)	45.5	66.4
HF Yield, %	86.3	

The yield obtained for distillation is appreciably lower due to decomposition during the distillation.

15 Examples 6-12 Fluorination of Acetone
 With Different Porous Tubes

Example 5 was repeated for shorter runs with the effluent analyzed by on-line gas chromatography. In Examples 6-8 a porous stainless steel (SS) tube with 0.5 micrometer pore size was used. In Examples 9-11 a porous nickel (N) tube with 5 micrometer pore size was used. Both tubes have substantially the same external dimensions and thickness as the Inconel (I) tube used in Examples 1-5 and also in Example 12. The feed rates into the inner zone (IZ) and annular zone (AZ), contact times, maximum temperature measured by the thermowell and product analyses (by area % normalized to exclude unreacted acetone and sulfur hexafluoride) are all shown in Table 3. Also shown is the HF in the effluent as a percentage of the theoretical value obtained by assuming that each fluorine molecule fed was involved in the stoichiometry $R-H + F_2 \longrightarrow R-F + HF$.

Table 3

	<u>Example</u>	<u>6</u>	<u>7</u>	<u>8</u>	
	Tube	SS	SS	SS	
5	IZ Flow (F ₂ /SF ₆)	0.09/0.5	0.3/1.0	0.15/0	
	AZ Flow (Acetone/SF ₆)	0.32/0.61	0.32/0.61	0.29/1.61	
	Contact Time (S)	12.6	7.3	8.5	
	Max. Temp. (°C)	100	185	141	
10	GC Analysis (%) CF ₃ COCF ₃	62	9	9	
	Other Fluoro- Acetones	14	67	10	
	CF ₄	18	18	61	
15	COF ₂ *	6	6	20	
	HF (% of Theory)	90	-	79	
	<u>Example</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
	Tube	N	N	N	I
20	IZ Flow (F ₂ /SF ₆)	0.13/1.0	0.24/1.0	0.24/1.0	0.25/2.0
	AZ Flow (Acetone/SF ₆)	0.30/0.61	0.30/0.61	0.30/0.30	0.30/0.61
	Contact Time (S)	5.4	7.5	8.6	5.4
	Max. Temp. (°C)	85	113	122	136
25	GC Analysis (%) CF ₃ COCF ₃	65	49	20	62
	Other Fluoro- Acetones	19	11	5	20
	CF ₄	12	30	51	13
30	COF ₂ *	4	10	18	5
	HF (% of Theory)	76	-	100	83

*The COF₂ value is estimated because of interference between the COF₂ peak and the SF₆ peak in the analysis.

Example 8 represents a less preferred mode of the process in which acetone, but not fluorine, was admixed

with sulfur hexafluoride before feeding into the reactor. This example produced the highest proportion of cleavage products (CF_4 and COF_2). Examples 6, 9 and 12 represent the more preferred modes of the invention where the

5 fluorine to sulfur hexafluoride molar ratio fed to the inner zone is between about 1:5 and about 1:10 (1:5.5, 1:7.7 and 1/8 respectively). Examples 7, 10 and 11 have slightly less preferred molar ratios of fluorine to sulfur hexafluoride (1:3.3, 1:4.2 and 1:4.2

10 respectively) which is still within the broader range of between about 2:1 and about 1:12.

Comparative Examples 13 and 14

Fluorination of Methanes

Using an Inconel porous tube with 10 micro-

15 meter pore size, and otherwise the same apparatus as in Example 1, methane was fluorinated using nitrogen as the diluent. CF_4 , but no partially fluorinated methanes were observed in the effluent by on-line gas chromatography. In Comparative Example 13 the total feeds were 0.5 mol/h

20 of fluorine, 0.45 mol/h of methane and 0.5 mol/h of nitrogen. The respective feeds in Comparative Example 14 were 0.1, 0.4 and 0.5 mol/h. The maximum temperatures observed by the thermowell were 52°C and 69°C, respectively. Calculated yields were 88% and 84% tetrafluoro-

25 ethane, respectively. This comparative example indicates that if one were to apply the teachings of Canadian Patent 990,738 directly to fluorination of methane, reactivity would be observed with a conventional nitrogen diluent.

Comparative Examples 15 and 16

Fluorination of Ethane

Several attempts were made to fluorinate ethane with fluorine using nitrogen as the diluent. Two such examples are described herein. Using the Inconel

35 porous tube described above, 0.5 mol/h of ethane was fed into the outer zone of the reactor and 0.1 mol/h of F_2 diluted with 0.5 mol/h of nitrogen was fed into the annular zone. Maximum temperature observed was 74°C.

Gas chromatographic analysis of effluent showed no C_2F_6 but essentially all CF_4 . The yield of the latter agreed with F_2 introduced. The experiment was repeated except that the reaction was immersed in a cooling bath to give
5 an internal temperature of about -50° . The results were the same as the preceding.

Comparative Example 17

An attempt was made to fluorinate acetone with fluorine, diluting each with sulfur hexafluoride,
10 in a pipe reactor. A cylindrical stainless steel pipe one inch (2.5 cm) inside diameter by 12 inch (30 cm) length was packed with 27.5 g copper mesh. Streams of 0.07 mol/h of fluorine diluted with 0.5 mol/h of sulfur hexafluoride and 0.25 mol/h of acetone diluted with 0.61
15 mol/h of sulfur hexafluoride were fed into the bottom end and the effluent from the top end was analyzed by on-line gas chromatography. The maximum temperature sensed by a thermowell along the center of the reactor was $100^\circ C$. Partially fluorinated acetones, but no
20 CF_3COCF_3 and no CF_4 were detected in the effluent.

Comparative Example 18

When Comparative Example 17 was repeated at higher flow rates of fluorine and consequently higher temperatures, increasing amounts of both CF_3COCF_3 and
25 CF_4 were observed. Several runs are plotted in Table 4. This example shows that, while some benefits can be achieved by using SF_6 as a diluent in a pipe tube reactor, higher amounts of cleavage products are obtained compared to CF_3COCF_3 than in the porous tube
30 reactor process employed in Examples 5-12.

Table 4Fluorination of Acetone in Pipe Reactor

Run	17	18A	18B
F ₂ /SF ₆ flow (mol/h)	0.07/0.50	0.13/0.50	0.25/0.50
5 Acetone/SF ₆ flow (mol/h)	0.25/0.61	Same	Same
Contact Time (s)	17.2	16.4	15.3
Max. Temp. °C	100	170	250
10 <u>GC Quantitative</u> <u>Analysis</u>			
CF ₃ COCF ₃	nil	low	nil
Other Fluoro- Acetones	high	medium	low
CF ₄ and COF ₂	low	medium	high

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We claim:

1. A process for fluorinating acyclic organic compounds which comprises:

a) passing fluorine as a first gaseous reactant into an elongated inner zone surrounded by a porous metal member which is substantially resistant to fluorine corrosion, and

b) introducing as a second gaseous reactant outside the porous metal member an organic compound having at least two carbons with at least one fluorinatable carbon selected from the group consisting of carbons covalently bonded to H, Cl or Br and carbons olefinically or acetylenically bonded to other carbons;

the pressure in said elongated inner zone being greater than the pressure outside the porous metal member;

at least one of said first and second gaseous reactants being admixed with a per-fluorinated gaseous diluent selected from the group consisting of sulfur hexafluoride, tetrafluoromethane, hexafluoroethane and octafluoropropane.

2. The process of claim 1 wherein said per-fluorinated gaseous diluent is sulfur hexafluoride.

3. The process of claim 2 wherein said first and second gaseous reactants are each admixed with sulfur hexafluoride.

4. The process of claim 3 wherein the mole ratio of fluorine to sulfur hexafluoride admixed therewith is between about 2:1 and about 1:12 and the mole ratio of second gaseous reactant to sulfur hexafluoride admixed therewith is between about 4:1 and about 1:5.

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5. The process of any previous claim wherein the porous tube has a pore size of between about 0.5 and about 50 micrometers.

5 6. The process of any previous claim wherein said second gaseous reactant is an acyclic hydrocarbon of 2-8 carbons having at most one olefinic unsaturation.

7. The process of any previous claim wherein the second gaseous reactant has three carbons.

10 8. The process of claim 7 wherein the second gaseous reactant is propane or propene.

9. The process of claim 7 or 8 wherein between 50 and 150 percent of the stoichiometric amount of fluorine is used.

15 10. The process of any of claims 1-5 or 7 wherein said second gaseous reactant is a ketone of 3-8 carbons.

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European Patent
Office

EUROPEAN SEARCH REPORT

0032210

Application number

EP 80 10 7844

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
AD	CA - A - 990 738 (ALLIED CHEMICAL CORP.)		C 07 B 9/00 B 01 J 12/00 B 01 J 19/24// C 07 C 19/08 49/167
A	DE - C - 651 049 (I.G. FARBEN-INDUSTRIE)		
AD	CHEMICAL ABSTRACTS, vol. 80 1974, page 371, abstract 95458u Columbus, Ohio. USA & JP - A - 74 00201 (DAIKIN KOGYO CO.LTD.) (05-01-1974)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 07 B 9/00 C 07 C 17/10 45/63 B 01 J 12/00 B 01 J 19/24
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
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The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	25-03-1981	VAN GEYT	